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**MASTER**

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Some Experimental Work Related to Two Bismuth Sulfate Cycles and  
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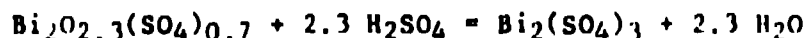
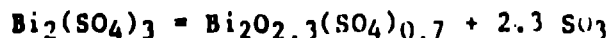
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Introduction

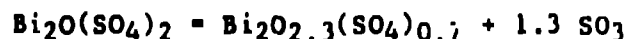
Work on a bismuth sulfate hybrid thermochemical cycle began with the suggestion by M. G. Bowman that some of the problems of heat penalty and corrosion associated with the use of solutions in thermochemical hydrogen cycles might be decreased by the use of solids of low solubility which could be decomposed at high temperature and that this notion could be applied to sulfuric acid cycles by forming a sulfate from the  $H_2SO_4$ . Ideally the sulfate should have low solubility, few or no waters of hydration, and decompose at not too high temperatures. Bismuth sulfate seemed suitable for investigation.

Two bismuth sulfate cycles are made possible by the stepwise decomposition of the sulfate-oxysulfate system. Omitting statement of the steps for decomposition of  $SO_3$  and the electrochemical formation of  $H_2$  and  $H_2SO_4$  from  $SO_2$  and  $H_2O$ , the key reactions are:

Cycle I



Cycle II

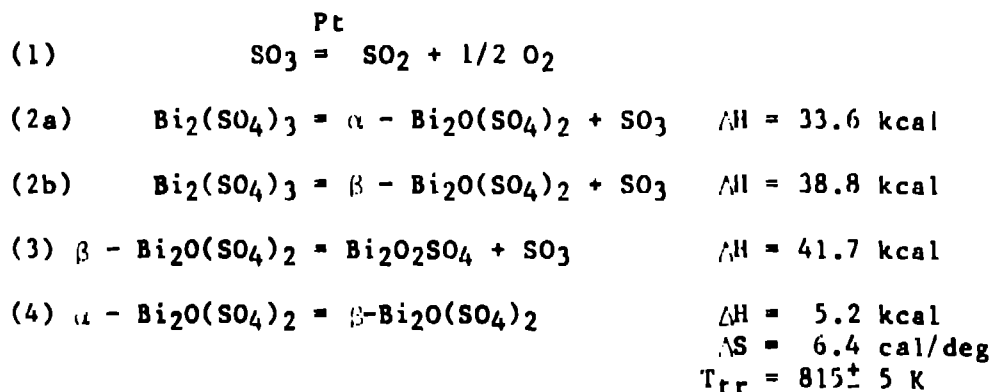


Cycle I proceeds through the intermediate oxysulfates  $Bi_2O(SO_4)_2$  and  $Bi_2O_2SO_4$  and Cycle II through  $Bi_2O_2SO_4$ . Cycle I has the advantage of generating 2.3 moles of  $H_2$  per mole of  $Bi_2O_3$ , compared with 1.3 for Cycle II. Published work<sup>1</sup> on the  $Bi_2O_3$ - $SO_3$ - $H_2O$  system shows that  $Bi_2(SO_4)_3$  is the stable solid in contact with  $H_2SO_4$  solutions above 52.7 wt%, so that acid of at least this strength would have to be used in Cycle I. Concentrations between about 3 wt% and 52.7 wt% could be used for Cycle II. The efficiency for electrochemical formation of  $H_2SO_4$  and  $H_2$  seems at present to be a maximum at around 30 wt%  $H_2SO_4$ .

Some thermodynamic data obtained for the decomposition reactions will be presented. A possible improvement in these cycles will be discussed which may provide a solution to a problem of sorption of  $H_2SO_4$  solution by the solids and might allow use of a more dilute acid than in Cycle I above.

## Equilibrium Pressures in the Decomposition of $\text{Bi}_2(\text{SO}_4)_3$ and $\alpha$ - and $\beta$ - $\text{Bi}_2\text{O}(\text{SO}_4)_2$

Work has been completed<sup>2</sup> on determination of equilibrium total pressures in closed systems for the first two stages of dissociation. Platinum black was mixed with the solids to establish equilibrium (1), and the known  $K_1$  was used to obtain the equilibrium  $\text{SO}_3$  pressures for (2) and (3). The data are shown in Figs. 1 and 2. There is a transformation of  $\text{Bi}_2\text{O}(\text{SO}_4)_2$  at  $T_{\text{tr}} = 815 \pm 5 \text{ K}$



between a low temperature  $\alpha$  and high temperature  $\beta$  form. The transformation is unusually sluggish, allowing equilibrium pressures for (2b) involving metastable  $\beta$  to be measured below  $T_{\text{tr}}$ . Pressures for (2a) were obtained after  $\beta$  had very slowly transformed in situ to stable  $\alpha$  below  $T_{\text{tr}}$ . The  $\beta$  form had been found from a new x-ray diffraction pattern observed when  $\text{Bi}_2\text{O}(\text{SO}_4)_2$ , made outside the equilibrium apparatus by thermal decomposition of  $\text{Bi}_2(\text{SO}_4)_3$ , was annealed at a higher than usual temperature. Time-temperature characteristics of the transformation and an independent value of  $T_{\text{tr}}$  were then determined by annealing and x-ray powder diffraction. The form appears to be stable indefinitely at room temperature. The transformation should not affect a cycle importantly but would have to be allowed for. Additional crystal forms have not been found for the other components in (2a), (2b), and (3).

### Survey Experiments on the Thermal Decomposition of $\text{Bi}_2(\text{SO}_4)_3$

Survey experiments on the decomposition of  $\text{Bi}_2(\text{SO}_4)_3$  in flowing helium showed breaks in decomposition rate after evolution of one mole of  $\text{SO}_3$  at 1050 K and after two moles at 1150 K. At 1240 K the abrupt decrease in rate, after less than two minutes reaction time, took place after evolution of 2.3 moles. Further evolution at 1240 K was very slow, leading to formation of a liquid phase (eventually  $\text{Bi}_2\text{O}_3(l)$ ), and would require excessive heat input. Process development work at Los Alamos<sup>3,4,5</sup> has included the use of a bench-scale rotary kiln to study the rapid decomposition reaction of Cycle II and several other decompositions. These experiments, along with the thermodynamic data presented for the first two stages of dissociation and the likelihood that no unusually large enthalpy change will be involved in going from  $\text{Bi}_2\text{O}_2\text{SO}_4$  to  $\text{Bi}_2\text{O}_{2.3}(\text{SO}_4)_{0.7}$ , determine the two cycles that are practically possible.

The gas evolved by the solid at each of the above temperatures was at least 99%  $\text{SO}_3$ , although extensive dissociation would have taken place at thermodynamic equilibrium.  $\text{SO}_3$  is then the species emerging from the normal sulfate and the first two oxysulfates. These solids were not

catalysts for  $\text{SO}_3$  dissociation within the 0.25 minute residence time. They would also not be catalysts for recombination of  $\text{SO}_2 + 1/2 \text{O}_2$ .

The need in these cycles for heat at high temperatures to dissociate  $\text{SO}_3$  and for heat over a range of lower temperatures in the stagewise decomposition of the solid makes the cycles candidates for use with a high-temperature, gas-cooled reactor. The fact that the solids are not catalysts for  $\text{SO}_3$  dissociation would give some flexibility in matching heat requirements to heat availability. If desired, a catalyst could be mixed with the solid (if compatible with it and the rest of the cycle), or could be located independently. Decomposition of the solid would be more extensive if it gave equilibrium  $\text{SO}_2 + 1/2 \text{O}_2$  pressures than if it gave equilibrium  $\text{SO}_3$  pressure only.

#### Hydrates. Sorption of $\text{H}_2\text{SO}_4$ Solutions by the Solids. Possible Improvement of the Cycles

The conclusion of Urazov et al.<sup>1</sup> was initially accepted that anhydrous  $\text{Bi}_2\text{O}(\text{SO}_4)_2$  was the stable phase in contact with  $\text{H}_2\text{SO}_4$  solutions between 3 and 52.7 wt%, although previous preparative<sup>6</sup> work indicated that mono- and trihydrates could be formed. Later, two new x-ray patterns were observed with samples of  $\text{Bi}_2\text{O}(\text{SO}_4)_2$  known to have been exposed to moisture. A sample of  $\text{Bi}_2\text{O}(\text{SO}_4)_2$  prepared from  $\text{Bi}_2\text{O}_3$  in 1-2 M  $\text{H}_2\text{SO}_4$  and dried with acetone and by mild heating in vacuum (preparation by C. L. Peterson), showed one of these patterns. This pattern was changed to the second pattern after evolution of two moles of water at 275°C. After much slower evolution of a third mole of water at 275°C the pattern was that of anhydrous  $\alpha\text{-Bi}_2\text{O}(\text{SO}_4)_2$ . The trihydrate is regularly formed in preparations from  $\text{Bi}_2\text{O}_3$  and 3M  $\text{H}_2\text{SO}_4$  for kiln decompositions.<sup>4</sup>

Attention had earlier been drawn to occlusion of  $\text{H}_2\text{SO}_4$  by  $\text{Bi}_2\text{O}(\text{SO}_4)_2$  (actually by the trihydrate) when the latter was formed by adding  $\text{Bi}_2\text{O}_3$  powder to stirred 1M  $\text{H}_2\text{SO}_4$ ; the observed final 0.8 M  $\text{H}_2\text{SO}_4$  corresponded to the expected reaction. After centrifuging, the solid was dried at 280°C to constant weight. The final weight and x-ray diffraction pattern unexpectedly corresponded to  $\text{Bi}_2(\text{SO}_4)_3$ . Estimates showed that about 10% more  $\text{H}_2\text{SO}_4$  had been present in the wet solid than was necessary, upon concentration during heating, to give trisulfate. Since the sorbed solution had about 75 moles  $\text{H}_2\text{O}$  per mole of solid, the behavior had no value as a method of making trisulfate. Later, C. L. Peterson, in making material under approximately the same conditions for decomposition in a fluidized bed, was able to reduce the amount of sorbed solution greatly, in one case to 8.8 moles  $\text{H}_2\text{O}$  per mole of solid. If we assume that incorporation of only 8 moles of  $\text{H}_2\text{O}$  per mole of product can be achieved - three as hydrate and five as sorbed solution - then if the solution were 11.1 m (52.1 wt%), enough  $\text{H}_2\text{SO}_4$  would be present to give trisulfate for a cycle I process. Heat would have to be provided to vaporize 9 moles of water, but only 4.5 moles per mole of  $\text{H}_2$ . While the acid concentration could be somewhat lower than required for a direct cycle I, in which stronger than 52.7 wt% acid would be needed to avoid circulation of an excessive volume of solution, a major advantage of this way of implementing cycle I would be the elimination of the sorbed solution problem, with its heat penalty. It would be necessary that the high temperature product

$\text{Bi}_2\text{O}_3(\text{SO}_4)_{0.7}$  be sufficiently active to react with the  $\text{H}_2\text{SO}_4$  to give trisulfate before vaporization of the acid and that the trisulfate have suitable characteristics for kiln operation. Other extents of sorption would change the amount of  $\text{H}_2\text{O}$  to be vaporized (the volume of solution sorbed per mole of trihydrate may be a function of acid concentration).

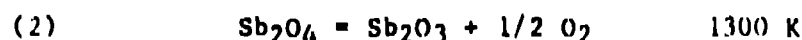
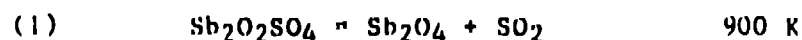
The morphology and relatively large particle size of  $\text{Bi}_2\text{O}(\text{SO}_4)_2$  developed to give good characteristics for kiln operation come from a filter cake of trihydrate with about 10 moles of water per mole of solid.<sup>4</sup> The sorted solution corresponds to seven waters and 0.36  $\text{H}_2\text{SO}_4$ 's per mole of solid (2.88 m, 22 wt% final  $\text{H}_2\text{SO}_4$ ). If this  $\text{H}_2\text{SO}_4$  all reacted to form trisulfate after concentration during heating, the final composition of the solid would be  $\text{Bi}_2\text{O}_{3-x}(\text{SO}_4)_x$  with  $x = 2.36$ . In practice  $x$  varied from 0 to 2.14.<sup>4</sup> Apparently the morphology and relatively large size of these particles did not allow much reaction before  $\text{H}_2\text{SO}_4$  vaporized.

Finally, it is possible that the formation of the trihydrate, although not of the monohydrate, could be avoided with the more concentrated  $\text{H}_2\text{SO}_4$  for a cycle I, as indicated by the experiments in Table I. The avoidance would be for kinetic reasons. It is assumed that  $\text{Bi}_2\text{O}_{2.3}(\text{SO}_4)_{0.7}$  would behave like the  $\text{Bi}_2\text{O}_3$  and  $\text{Bi}_2\text{O}(\text{SO}_4)_2$  in Table I. The heat penalty associated with two  $\text{H}_2\text{O}$ 's of hydration would be eliminated. Sorption characteristics of the monohydrate would be different from those so far observed, for the trihydrate.

The behavior of  $\text{Bi}_2(\text{SO}_4)_3$  and its decomposition products in a kiln are not known. Difficulties might be encountered in the preparation of material of suitable morphology, especially if one attempts to work through the intermediate  $\text{Bi}_2\text{O}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ , rather than the trihydrate.

#### Possible Simplification of the $\text{SO}_3$ - $\text{SO}_2$ - $\text{O}_2$ Separation Problem with a Sulfuric Acid-Antimonyl Sulfate Hybrid Cycle

Sulfuric acid-solid sulfate (or oxysulfate) cycles in which the metal ion has variable valence have the possibility of forming  $\text{SO}_2$  and a higher valence state oxide. The conditions on the sulfate outlined in the Introduction and decomposition of the oxide at reasonable temperatures to oxygen and a lower valent oxide (for reaction with  $\text{H}_2\text{SO}_4$ ) would be necessary. Decomposition of the sulfate to give both  $\text{SO}_2$  and  $\text{SO}_3$ , as is found with some first transition series sulfates, would not be of interest. This indicates the need to match the number of sulfates (say by choosing an oxysulfate) to the change in oxidation number of the metal ion. One possibility is antimonyl sulfate.



The temperature for (1) is suggested by the "glowing red" temperature at which Metz<sup>17</sup> decomposed  $\text{Sb}_2(\text{SO}_4)_3$  to  $\text{SO}_3$  and  $\text{Sb}_2\text{O}_4$ . Detailed conditions of the experiment were not given. No mention was made of  $\text{SO}_2$  formation,

$\text{Sb}_2\text{O}_3$  was apparently sometimes present, and some  $\text{Sb}_2\text{O}_4$  could have been formed by air oxidation of sesquioxide. However, in the event of decomposition to  $\text{Sb}_2\text{O}_3$  and  $\text{SO}_3$ , calculations show that  $\text{SO}_3$  should oxidize  $\text{Sb}_2\text{O}_3$  to  $\text{Sb}_2\text{O}_4$ . It would be necessary that no catalyzed dissociation of possible intermediate  $\text{SO}_3$  should take place.

The vapor pressure of  $\text{Sb}_2\text{O}_3(1)$  is relatively high at the temperature of (2); avoidance of back reaction and recovery of the heat of condensation would be necessary.

Hintermann and Venuto<sup>8</sup> report that anhydrous  $\text{Sb}_2\text{O}_2\text{SO}_4$  can be formed in boiling 6.5 M  $\text{H}_2\text{SO}_4$  (9.0 m, 47 wt%). The definite compound<sup>8,9</sup>  $\text{Sb}_6\text{O}_7(\text{SO}_4)_2$ , or  $\text{Sb}_2\text{O}_3 \cdot 2/3 \text{SO}_3$ , forms in the range 4.3 to 6.9 M at room temperature<sup>8</sup> or in 2.0 to 6.5 M in the boiling acid. If the solids sorb the  $\text{H}_2\text{SO}_4$  solution, it might be possible to solve this problem and use weaker acid then otherwise, as suggested for the bismuth cycles.

#### Acknowledgements

We thank Charles L. Peterson and Charles M. Hollabaugh for useful information and discussion, Mary Pretzel for x-ray work, and Willard Witteman for much helpful work in the classification of x rays.

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Table I

Hydration of  $\text{Bi}_2\text{O}_3 \cdot 2\text{SO}_3$  in more concentrated  $\text{H}_2\text{SO}_4$ 

Initial Solid	$\text{H}_2\text{SO}_4$ Concentration	Time	Temp., °C	Product
1. $\text{Bi}_2\text{O}_3$	50 wt% (44 wt% final)	3 h	25-40	$\text{Bi}_2\text{O}_3 \cdot 2\text{SO}_3$ (1.06 $\text{H}_2\text{O}$ ), from initial weight and product after EtOH extraction of $\text{H}_2\text{SO}_4$ and drying 6 h at 228°C.
2. $\alpha\text{-Bi}_2\text{O}_3 \cdot 2\text{SO}_3$	50 wt%	40 min	25-40	$\text{Bi}_2\text{O}_3 \cdot 2\text{SO}_3$ (0.97 $\text{H}_2\text{O}$ ); monohydrate x-ray pattern.
3. $\alpha\text{-Bi}_2\text{O}_3 \cdot 2\text{SO}_3$	50 wt%	6 h	75	$\text{Bi}_2\text{O}_3 \cdot 2\text{SO}_3$ (1.21 $\text{H}_2\text{O}$ ); monohydrate x-ray pattern.
4. $\alpha\text{-Bi}_2\text{O}_3 \cdot 2\text{SO}_3$	50 wt%	5 h	100	$\text{Bi}_2\text{O}_3 \cdot 2\text{SO}_3$ (1.88 $\text{H}_2\text{O}$ ); trihydrate and monohydrate x-ray patterns.
5. $\alpha\text{-Bi}_2\text{O}_3 \cdot 2\text{SO}_3$	1 m.	10 min	25	$\text{Bi}_2\text{O}_3 \cdot 2\text{SO}_3$ (3.1 $\text{H}_2\text{O}$ ); trihydrate x-ray pattern.
	44 wt% followed by	5 h	75	



